

PREPARATION AND PROPERTIES OF
MONODISPERSE BRANCHED POLYSTYRENE

M. Morton, T. E. Helminiak, S. D. Gadkary and F. Bueche

INSTITUTE OF RUBBER RESEARCH
UNIVERSITY OF AKRON

ABSTRACT

Model branched polymers have been prepared by the reaction of relatively monodisperse polystyryl lithium with silicon tetrachloride. The branched molecules have been carefully characterized by light scattering and osmotic pressure measurements. A study of the dilute solution properties of the branched molecules has confirmed the theoretical development of the branching coefficient, g' , by Zimm and Kilb. The second virial coefficient, A_2 , has been found to decrease with increased branching. In addition, the Huggins constant, k' , has been found to be a poor measure of branching in molecules.

INTRODUCTION

Zimm and Kilb¹ have presented theoretical formulas for the intrinsic viscosity and viscoelastic properties of some model branched molecules in dilute solution. Using their theoretical expression, they were able to calculate the ratio of the intrinsic viscosities of several model branched molecules to that of linear molecules having the same molecular weight. This ratio is expressed by the following equation,

$$g' = \frac{[\eta]_b}{[\eta]_l}$$

Although they referred to data available in the literature to substantiate the validity of their work, the inherent uncertainties in the branched polymer characterizations detracted from the test of the mathematical treatment.

In order to resolve this uncertainty, it was the purpose of this work to prepare well-characterized model branched polymers and study their dilute solution behavior. The unique characteristics of anionic polymerization lend themselves very well to the purpose intended. The anionic polymerization of styrene can be used to prepare relatively homogeneous linear polymer of predetermined molecular weight. In addition, the "living" nature of the polystyryl anion can be used to further advantage in the preparation of the branched molecules. In this work, the polystyryl anion was reacted with silicon tetrachloride to yield molecules with three and four uniform branches emanating from a single point. These "star" type molecules were then used to experimentally

Report Documentation Page				Form Approved OMB No. 0704-0188	
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
1. REPORT DATE 1962		2. REPORT TYPE		3. DATES COVERED 00-00-1962 to 00-00-1962	
4. TITLE AND SUBTITLE Preparation and Properties of Monodisperse Branched Polystyrene				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Paul V. Galvin Library, 35 W. 33rd Street, Chicago, IL, 60616				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT Model branched polymers have been prepared by the reaction of relatively monodisperse polystyryl lithium with silicon tetrachloride. The branched molecules have been carefully characterized by light scattering and osmotic pressure measurements. A study of the dilute solution properties of the branched molecules has confirmed the theoretical development of the branching coefficient, g, by Zimm and Kilb. The second virial coefficient, A_2, has been found to decrease with increased branching. In addition, the Huggins constant, k', has been found to be a poor measure of branching in molecules.					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Same as Report (SAR)	18. NUMBER OF PAGES 10	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

determine the g' factor, the second virial coefficient, A_2 , and the Huggins constant, k' .

EXPERIMENTAL

Preparation of Linear Polystyrene

In order to prepare model branched compounds consistent with the models used in the calculations of Zimm and Kilb, it was necessary to prepare relatively monodisperse linear polystyrene. To accomplish this task, styrene monomer was polymerized using anionic polymerization techniques under high vacuum [10^{-6} mm Hg]. The details concerning purification of solvent and monomer and the use of catalyst seed have been described elsewhere². The polymerization apparatus is shown in Figure 1 and the procedures used, with exception of one modification, have already been described². The modification consisted of distilling the styrene monomer from the ampoule into the frozen benzene seed solution in flask F_1 (see Figure 1). This distillation insured the addition of pure monomer to the reaction flask, whereas the freezing of the mixture prevented polymerization during distillation. After thawing, the monomer-seed solution was thoroughly mixed and a substantial portion was transferred to flask F_2 . Having transferred some of the solution, flask F_2 was cut away. The solutions in both flasks were kept at room temperature for 24 hours with continuous stirring. The polymerization was considered complete after the 24 hour interval.

In order to determine the molecular weight of the linear polymer prepared in this manner, the catalyst concentration of the polymer in flask F_1 was determined by titrating the orange colored polystyryl anions with a standard *n*-butanol solution by means of a slow-leaking burette, B (see Figure 1). The butanol termination of the polystyryl anions caused a loss of color, and thus the titration end-point was a colorless solution. After titration, the polymer was precipitated from solution with methanol, filtered, dried and weighed. Hence, from the weight of polymer and the number of moles of catalyst, it was possible to estimate the molecular weight of the linear polymer. This linear polymer is referred to as the S_{10} sample.

Preparation of Branched Polystyrene

The polymer remaining in flask F_2 was used to prepare the branched molecules. Knowing the amount of monomer initially used, and the weight and molecular weight of the polymer in flask F_1 , it was possible to calculate, by difference, the number of moles of polymer in flask F_2 . To this flask was added a less than equivalent amount of silicon tetrachloride calculated on the assumption that all four chlorines would be replaced by polystyryl anions. The excess of polystyryl anions was necessary to insure that the linking reaction would go to completion.

The silicon tetrachloride used in the linking reaction was treated in the following manner. It was dried over anhydrous sodium sulfate and distilled twice before collecting into weighed ampoules. Benzene solutions were made and the concentration of silicon tetrachloride was determined by breaking an ampoule in ice water and titrating the liberated hydrochloric acid with standard sodium hydroxide solution using phenolphthalein as an indicator.

Having introduced the silicon tetrachloride into the polymer solution, the mixture was allowed to stand for 48 hours at 50°C. At the end of this period, any remaining polystyryl anions were terminated by the addition of n-butanol. The resulting polymer mixture was precipitated in methanol, dried, and weighed. This polymer sample is referred to as the 4S₁₀ sample.

Polymer Characterization

The polymer sample 4S₁₀, which was the total polymer product of the linking reaction of polystyryl-lithium and silicon tetrachloride, was initially expected to contain the tetra-linked star molecules and the excess linear polymer S₁₀. Hence, fractionation was considered necessary to isolate the pure, linked product. However, careful fractionation became even more important when, in initial attempts at preparing the linked products, it was observed that mixed products of tetra- and tri-linked molecules were being formed.

Fractionation

The mixed polymer product, 4S₁₀ was dissolved in benzene to give a 0.12% solution by weight. The non-solvent used for the fractionation was methanol. The fractionation was carried out at a constant temperature of 30°C. Upon separation, the fractions were precipitated in methanol, dried in vacuo, and weighed. The weight fraction data for the fractionation are listed in Table I.

Molecular Weight Determinations

In order to establish the efficiency of fractionation, the degree of linking and the homogeneity of both linear polymer and the fractions, it was necessary to determine both the weight- and number-average molecular weights of the samples. To obtain this information, osmotic pressure and light scattering measurements were made.

The light scattering measurements were made using a Brice-Phoenix light scattering photometer, Universal 1000 series. Calibration was accomplished through the use of a reference standard opal provided with the instrument. In order to recheck the calibration, the absolute turbidity of benzene was determined, and it agreed to 0.6% with the value listed by Carr and Zimm³. All the solutions were filtered through sintered glass frits to remove insoluble impurities. The scattering intensities of the solutions

were determined at various angles through the use of a cylindrical cell having the dimensions, 75 x 26 mm. The scattering system was a polystyrene-benzene solution and the refractive index increment for a wave-length of 436 millimicrons was $0.1151 \text{ ml gm}^{-1}$. The data obtained were interpreted through the use of a Zimm plot. The weight-average molecular weights thus obtained are listed in Table I.

The number-average molecular weights were obtained through osmotic pressure measurements. The osmometers used were of the design developed by Immergut and Stabin⁴. The membranes used were gel cellophane, grade No. 600. The osmotic molecular weight of the linear S_{10} sample was determined in benzene solution at 30°C . For fractions, A-4 S_{10} and B-4 S_{10} , the measurements were made in butanone at 25°C . All the osmotic pressures were obtained by the static method and the equilibrium times were of the order of 20 hours. The number-average molecular weights are listed in Table I.

Viscosity Determinations

In order to obtain g' , it was necessary to experimentally determine the intrinsic viscosity of the branched molecules. The viscosities were determined in two solvents, toluene at 25°C and cyclohexane at 34°C , the former being a good solvent and the latter a theta, Θ , solvent. The measurements were made using a Ubbelohde dilution viscometer having a flow time of 123 sec. for toluene and 193 sec. for cyclohexane, and having a negligibly small kinetic energy correction.

RESULTS AND DISCUSSION

The fractionation data and weight-average molecular weight values are listed in Table I. The agreement between the weight-average molecular weight of 4 S_{10} which was determined experimentally to be 1.93×10^5 , and the calculated value of 1.90×10^5 for this sample calculated from the data for the individual fractions, indicates that the fractionation was efficient and complete. However, to insure that the fractions were homogeneous, number-average molecular weights were determined (see Table I) and were used to determine the heterogeneity ratio, M_w/M_n , for the A-4 S_{10} and B-4 S_{10} samples. In addition, the heterogeneity ratio was determined for the linear S_{10} sample. The ratios obtained indicated that the fractionation was indeed very efficient and that both fractions of the linked polymer and the linear polymer were homogeneous enough for the purposes intended.

Having established the fact that homogeneous fractions were obtained, it was still necessary to determine the degree of branching that had taken place to produce each fraction. This was done by calculating the linking ratio, i.e., the number-average molecular weight of the branched molecule divided by the number-average

TABLE I

Fractionation and Molecular Weight Data

Sample	Weight Fraction	$\bar{M}_w \times 10^5$	$\bar{M}_n \times 10^5$	$\frac{\bar{M}_w}{\bar{M}_n}$	$\frac{4S-\bar{M}_n}{S-\bar{M}_n}$
S_{10}	-	0.606	0.574	1.06	-
$4S_{10}$	-	1.93	-	-	-
A- $4S_{10}$	0.252	2.57	2.35	1.09	4.09
B- $4S_{10}$	0.349	1.70	1.70	1.00	2.96

molecular weight of the linear sample, S_{10} , i.e. $4S_{10}-\bar{M}_n/S_{10}-\bar{M}_n$. The reasons for using the number-averages to determine the degree of linking are given in the Appendix, where the effects of molecular weight distribution are considered. In the case of the A- $4S_{10}$ sample, the ratio was, within experimental error, 4.0, whereas for B- $4S_{10}$ the ratio was 3.0, as shown in Table I. Thus, having shown the linear polymer to be relatively homogeneous, and having demonstrated the separation of homogeneous branched polymers it can be assumed that the A- $4S_{10}$ sample is a "star" type molecule with four branches, of essentially the same length, emanating from a single point. The B- $4S_{10}$ sample is a "star" with three such branches.

Viscosity measurements were made for both branched polymers in toluene at 25°C, a good solvent, and in cyclohexane at 34°C, the theta solvent. The data are listed in Table II. In order to determine the branching coefficient, g' , as defined by Zimm and Kilb¹, it was necessary to obtain the intrinsic viscosity of a linear polymer having the same molecular weight as each of the branched polymers. It was originally intended to calculate these values using the viscosity-molecular weight relationship reported by Outer, Carr and Zimm⁵ for polystyrene-toluene at 25°C. However, the linear polymer prepared by anionic polymerization in benzene did not exactly obey the equation reported by Outer, Carr and Zimm⁵. The viscosities experimentally determined were observed to be consistently lower than those calculated from the literature equation. Therefore, it was necessary to establish the viscosity-molecular weight equation experimentally. The equation determined for toluene at 25°C was as follows,

$$[\eta] = 1.46 \times 10^{-4} \bar{M}_w^{0.69}$$

The reason for the slight difference between this equation and that reported by Outer, Carr and Zimm is unknown at the present time. There is a remote possibility that there is a consistent error in these measurements. However, the procedure used herein eliminates any error in the g' calculations.

In order to calculate the viscosity of the linear polymer in cyclohexane at 34°C, it was necessary, due to the discrepancy observed in toluene, to apply a proportionate correction to the viscosity-molecular weight equation reported for cyclohexane at 34°C by Krigbaum and Flory⁶. The equation determined for these polymers is as follows,

$$[\eta] = 7.45 \times 10^{-2} M^{0.5}$$

The viscosities calculated, using the above equations for linear molecules of the same molecular weight as the branched molecules, are listed in Table II. The ratios of the branched to linear intrinsic viscosities for both toluene and cyclohexane have been calculated and the agreement between the experimentally and theoretically determined g' factors is very favorable (see Table II). Thus, within the degrees of experimental error involved, this viscosity study lends considerable support to the theoretical work of Zimm and Kilb.

TABLE II

Viscosity Data

Polymer	$[\eta]_b$ Expt.		$[\eta]_l$ Calc.		g' Expt.		g' Theory
	$*C_7H_8$	C_6H_{12}	C_7H_8	C_6H_{12}	C_7H_8	C_6H_{12}	
A-4S ₁₀	70.5	30.9	84.0	37.8	0.84	0.82	0.81
B-4S ₁₀	56.3	28.8	63.0	30.7	0.90	0.94	0.91

$[\eta]$ - ml gm⁻¹

$[\eta]_l$ - linear

$[\eta]_b$ - branched

*Toluene at 25°C, cyclohexane at 34°C.

The second virial coefficient, A_2 , was obtained for the branched molecules in benzene and butanone. The A_2 values in benzene were obtained from light scattering data, whereas the values in butanone were obtained from osmotic pressure measurements. The A_2 values for linear molecules corresponding to the molecular weights of A-4S₁₀ and B-4S₁₀ were obtained from a plot of the log A_2 vs. log \bar{M}_w for linear molecules (see Table III). From the data, it can be observed that, in going from linear to branched molecules, the A_2 value decreases. In addition, this decrease is proportionally greater when the degree of branching is increased. On changing from a good to poor solvent, the A_2 value is further decreased and, as would be expected, the difference in the A_2 values for A-4S₁₀ and B-4S₁₀, due to branching, becomes less obvious as the second virial coefficient decreases. These results are in agreement with theory and support the corresponding suggestions of Thurmond and Zimm⁷. It can be concluded that the second virial coefficient may be used as a qualitative measure of branching, but only in a good solvent.

TABLE III

Second Virial Coefficient Data

<u>Polymer</u>	<u>A₂ x 10³</u>		
	<u>Linear *</u> (Benzene)	<u>Branched</u>	
		Benzene	Butanone
A-4S ₁₀	0.54	0.33	0.19
B-4S ₁₀	0.57	0.49	0.19

TABLE IV

Huggins Constant Data

<u>Polymer</u>	<u>k'</u>		
	<u>Linear *</u> (Toluene)	<u>Branched</u>	
		C ₇ H ₈	C ₆ H ₁₂
A-4S ₁₀	0.31	0.38	0.85
B-4S ₁₀	0.31	0.41	0.88

* Determined for linear molecules having molecular weights corresponding to those of the branched polymers.

The Huggins constant, k' , was determined for the branched molecules, A-4S₁₀ and B-4S₁₀, and for linear molecules of the same molecular weights, in toluene at 25°C. In addition, the k' values were obtained in cyclohexane at 34°C for both branched samples (see Table IV). The data obtained indicate an increase in the k' value on going from linear to branched molecules and from good to poor solvents. In spite of this, the value of k' actually decreases when going from the less branched B-4S₁₀ to the more branched A-4S₁₀. Hence, it appears that k' does not behave in any simple way with degree of branching.

This is not unexpected when one notices that in the equation defining the Huggins constant,

$$\eta_{sp}/c = [\eta] + k' [\eta]^2 c.$$

The factor $k' [\eta]^2$ is the proper measure of intermolecular interference at concentration c . The quantity $[\eta]^2$ decreases or increases as the molecule shrinks or grows larger. It is the primary measure of the way in which the molecules will interfere with each other at a given concentration. The factor k' varies only slightly in comparison with $[\eta]^2$ and can be thought of as a correction factor necessary to compensate for small inaccuracies introduced by the use of the simple, but not rigorously correct,

factor $[\eta]^2$. It is to be expected that the variation of k' with branching and solvent power will not be understood until a very accurate theory for the concentration dependence of viscosity is available.

As the data indicate, even in a good solvent, the effect of branching on k' approaches the limits of experimental error. Thus the value of determining k' to establish the degree of branching is very limited. In addition to this fact, a dependence of k' on molecular weight has been reported by Cragg and Sones⁸, and this will further complicate the interpretation of k' values. Thus, because of these various limitations, k' becomes, at best, a very poor indication of the degree of branching.

CONCLUSIONS

The present studies have been successful in clarifying the following points: 1. Branched molecules of accurately determined form can be prepared by the methods used in this study. 2. The theory of Zimm and Kilb¹ for the intrinsic viscosity of branched molecules is valid. In addition, g' values are nearly the same for both good and poor solvents. 3. The value of the second virial coefficient, A_2 , is lower for a branched molecule than for a linear molecule of the same molecular weight. This effect is most easily observed in the case of good solvents. 4. Branching is not easily determined by measurement of the Huggins constant, k' . Although small changes are observed, they are not easily interpreted.

Since the molecules prepared for this study have been uniform and well characterized, other data in the literature, which may at times conflict with the above conclusions, should be used with caution.

REFERENCES

1. Zimm, B. H. and Kilb, R. W., J. Polymer Sci., 37 19 (1959)
2. M. Morton et al, J. Polymer Sci. (in press)
3. Carr, C. I. and Zimm, B. H., J. Chem. Phys., 18 1616 (1950)
4. Immergut, E. H. and Stabin, J. V., J. Polymer Sci., 14 209 (1954)
5. Outer, P., Carr, C. I., and Zimm, B. H., J. Chem. Phys., 18 830 (1950)
6. Krigbaum, W. R. and Flory, P. J., J. Polymer Sci., 11 37 (1953)
7. Thurmond, C. C., and Zimm, B. H., J. Polymer Sci., 8 477 (1952)

8. Cragg, L. H. and Sones, R. H., J. Polymer Sci.,
9 585 (1952)

LEGEND FOR FIGURE 1.

Polymerization Apparatus

- A - standard n-butanol solution ampoule
B - slow leaking burette
C₁ - catalyst seed for purging
C₂ - catalyst seed for polymerization
F₁ and F₂ - flasks with magnetic stirrers for
polymerization and linking reaction
F₃ - flask to remove purging solution
M - monomer ampoule
S - solvent ampoule
V - vacuum outlet

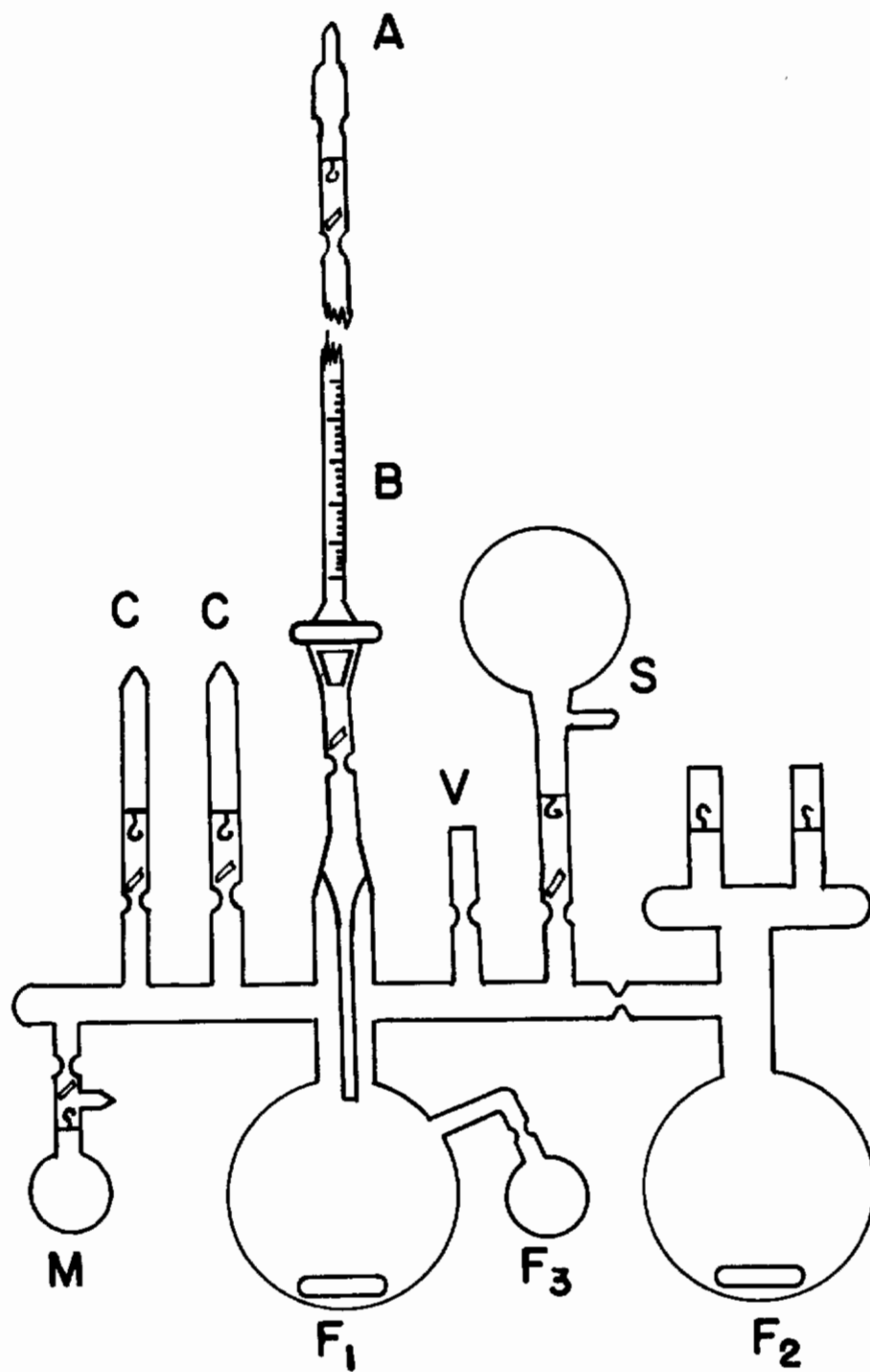


FIGURE 1 - POLYMERIZATION APPARATUS